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THE INFRA-RED SPECTRUM OF $\left[C_4H_4.Ag\right]$ NO_3

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IN this note we wish to report preliminary results from the analysis of the infra-red spectrum of cyclobutadiene silver nitrate $\left[C_4H_4Ag\right]$ NO_3[1] in relation to possible structures for the complex cation.

Table 1 shows the spectrum obtained with Unicam SP100 and Perkin-Elmer Model 21 spectrophotometers using LiF. NaCl and Cs Br optics and polycrystalline samples mulled in nujol, hexachlorobutadiene and fluorolube. Another spectrum obtained in a KBr disc showed evidence of decomposition of the complex.

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[1] M. Avram, E. Marica and C.D. Nenitzescu, Chem.Ber. 92, 1088 (1959).

The primary purpose of the investigation was to define the nature of the hydrocarbon ligand, and the first consideration is whether this has the formula C_4H_4 or C_8H_8. Dimeric structures have to be considered because a hydrocarbon of this formula is evolved on treatment of the complex with sodium chloride[2] and also because the overall spectrum is of some complexity. However whereas the silver nitrate complex shows only two bands in the ethylenic CH region, the evolved hydrocarbon shows a prominent third band in the saturated CH region[2,3] consistent with a suggested formula (I)[2]; an analogous formula for the hydrocarbon part of the complex therefore seems unlikely. The spectrum in the CH region would be consistent with an alternative structure involving co-ordinated cyclooctatetraene. There are, however, well defined differences between the spectrum as a whole and these of the cyclooctatetraene complexes $C_8H_8Fe(CO)_3$, $C_8H_8(CuCl)_2$ and $C_8H_8AgNO_3$. Although these differences are most pronounced in the regions of C=C stretching and out-of-plane CH angle deformation vibrations, and might

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[2] C.D. Nenitzescu (personal communication).

[3] L.J. Bellamy, Infra-red Spectra of Complex Molecules (2nd Edition) Methuen, London, 1958.

in part be explicable in terms of the different extent to which C=C bonds are coordinated to metal atoms,it seems on balance more likely that the structure is a monomeric one.

The complexity of the overall spectrum mentioned above is most evident in the skeletal and CH deformation regions[3], and is not found in these parts of the spectrum which are more readily interpreted in structural terms. The two bands in the CH region, one in the "C=C" region at 1479 cm^{-1} (it is possible, but not likely, that a second band is overlaid by the strong nitrate absorption below 1440 cm^{-1}), and one in the region expected for Ag-C vibrations at 474 cm^{-1}, all point to a structure that is not of great complexity and in which the Ag atom is linked in an equivalent fashion to each of the C=C bonds.

Before proceeding further it is necessary to consider the frequencies of the NO_3^- ion. Silver nitrate itself shows its fundamental infra-red bands at 1350 (V.S.), 807(S) and 738 cm^{-1} (M), the first and last of which correspond to doubly degenerate vibrations[4]. Two very

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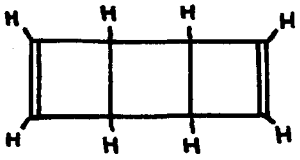
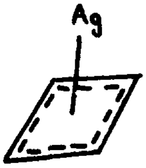
[4] G. Herzberg, Infra-red and Raman Spectra of Polyatomic Molecules. Van Nostrand, New York, 1945.

strong bands at 1385 and 1305 cm^{-1} in the spectrum of the complex correspond to the first of the NO_3- frequencies and the split degeneracy shows that the ion has probably been reduced in symmetry from D_{3h} to C_{2v} or less. In this situation the ca. 740 cm^{-1} band should also be split in the spectrum of the complex and the symmetrical N-O stretching frequency at ca. 1050 cm^{-1} becomes allowed. We therefore provisionally assign bands to the nitrate ion as indicated in the Table. There remain in the 1600 to 600 cm^{-1} region three strong bands at 1479, 936 and 827 cm^{-1}, three of medium intensity (1176, 1161 and 1042 cm^{-1}) and five weak bands for assignment to the hydrocarbon ligand, although the list may be incomplete because of the regions obscured by NO_3- absorptions, particularly between 1400 and 1250 cm^{-1}.

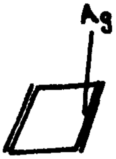
The spectroscopic data may now be considered in relation to possible structures for $[C_4H_4.Ag]^+$ ion. We shall discuss principally the four structures (II) to (V) based on a



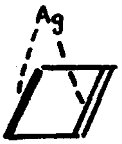
(I)



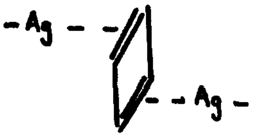
(II)



(III)



(IV)



(V)

Table 1: Infra-red frequencies of $[C_4H_4.Ag]NO_3$ in the solid state

(mulled in nujol, hexachlorobutadiene, and fluorolube)

3053	(W)	CH stretching
2994	(M)	
2304	(W)	NO_3^- combination (1059 + 1305)
1757	(W)	NO_3^- combination (718 + 1059)
1479	(S)	"C=C" stretching
1385	(VS)	NO_3^- (Asymm. NO stretching)
1305	(VS)	
1176	(M)	
1161	(M)	
1059	(W)	NO_3^- (Symm. NO stretching)
1042	(M)	
1006	(W)	
965	(W)	
936	(S)	
859	(W)	
842	(W)	
827	(S)	
814	(S)	NO_3^- (Out-of-plane deformation)
758	(M)	NO_3^- (in-plane deformation)
718	(W)	
641	(W)	
474	(S)	Ag-C stretching

(W) weak, (M) medium, (S) strong, and (VS) very strong bands.
The relative intensities only were estimated.

planar C_4H_4 unit. This type of formula accounts readily for the ethylenic type CH frequencies, and for the band at 1479 cm^{-1} which is in a very reasonable position for a C=C group of a 4-membered ring coordinated to a silver atom[5,6]. It is more difficult to account for the latter band, or for the Ag-C frequency of 474 cm^{-1}, on the basis of the tetrahedral C_4H_4 unit suggested by Lipscomb[7]; a higher C=C frequency would be expected for a C_4Ag 5-membered ring.

The structures(II) to (V) require 5, 14, 10 and 7 infra-red active fundamentals respectively in the 1600 500 cm^{-1} region[4] for comparison with six bands of considerable intensity and five weaker ones. Taking the

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[5] R.C. Lord and F.A. Miller, Applied Spectroscopy 10, 115 (1956).

[6] J. Chatt and L.A. Duncanson, J.Chem.Soc. 2939 (1953); D.B. Powell and N. Sheppard, Spectrochim.Acta. 13, 69 (1958); H.P. Fritz (unpublished work)

[7] W.N. Lipscomb, Tetrahedron Letters No.18, 20 (1959).

spectroscopic evidence at its face value a highly unsymmetrical structure such as (III) seems unlikely (particularly as it would require two C=C frequencies) and (IV) and (V) seem more probable. Strictly speaking (IV) also requires two C=C and Ag-C frequencies, but in this case it would be less surprising if one of each were weak. There are too many bands in the spectrum for the most symmetrical structure (II) to be present in the crystalline state. However it would perhaps be unwise to rule out this structure for a free ion in solution, as some of the spectral complexity may be the result of crystal distortions as for the nitrate ion. In summary, although a dimeric structure containing an ethylenic - type hydrocarbon ligand cannot entirely be ruled out on the basis of the spectroscopic evidence, the infra-red spectrum provides support for a monomeric formulation of $\left[C_4H_4.Ag\right]NO_3$ involving an essentially planar hydrocarbon ligand, with structure (V) as most probable on the spectroscopic evidence alone.

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